



# Synthesis, characterization, and crystal structure of hexakis(1-methyl-1*H*-imidazole- $\kappa$ N<sup>3</sup>)zinc(II) dinitrate

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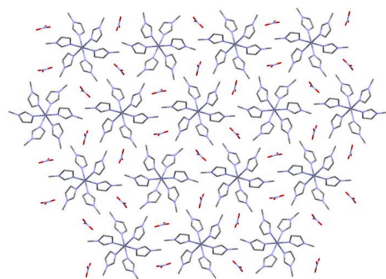
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The synthesis of the title compound, [Zn(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>, is described. This complex consists of a central zinc metal ion surrounded by six 1-methylimidazole ligands, charge balanced by two nitrate anions. The complex crystallizes in the space group  $P\bar{3}$ . In the crystal, the nitrate ions are situated within the cavities created by the [Zn(*N*-Melm)<sub>6</sub>]<sup>2+</sup> cations, serving as counter-ions. The three oxygen atoms of the nitrate ion engage in weak C—H...O interactions. In addition to single-crystal X-ray diffraction analysis, the complex was characterized using elemental analysis, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and FTIR spectroscopy.

## 1. Chemical context

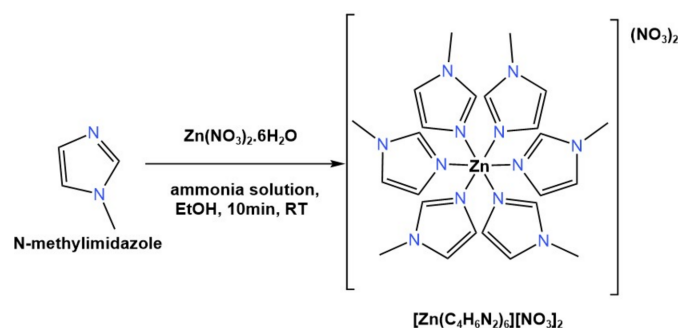
Extensive research has been conducted on zinc complexes containing imidazole and its derivatives due to their significance in chemistry and their diverse applications (Victor *et al.*, 2014; Porchia *et al.*, 2020). These complexes play crucial roles as anticancer agents (Porchia *et al.*, 2020; Babijczuk *et al.*, 2023), antibacterial agents (Guo *et al.*, 2022), fluorescent sensors (Anjali *et al.*, 2022), in anti-counterfeiting and latent fingerprint detection (Kempegowda *et al.*, 2021), and in materials chemistry (Rashamuse *et al.*, 2023; Bezvikonnyi *et al.*, 2022; Yu *et al.*, 2021). Notably, zinc is the second most prevalent trace metal in the human body and is essential in a variety of biological systems (Haase & Rink, 2014; Kolenko *et al.*, 2013). Consequently, it is unsurprising that Zn<sup>II</sup> ions demonstrate the ability to inhibit certain bacterial species (McDevitt *et al.*, 2011; Velasco *et al.*, 2018). The use of Zn<sup>II</sup> as the metal center in coordination chemistry is motivated by its ability to form strong complexes with ligands and the low cost of Zn precursors (Häggman *et al.*, 2020; Rashamuse *et al.*, 2023). In recent years, great efforts have been made to develop new organic zinc complexes with various architectures and applications (Abendrot, *et al.*, 2020; Brahma & Baruah, 2020; Chen *et al.*, 2021; Kseniya *et al.*, 2022; Loke *et al.*, 2020).

On the other hand, *N*-substituted imidazoles, or 1-substituted imidazoles, have emerged as highly attractive compounds due to a broad spectrum of applications (Chen *et al.*, 2020; Gu *et al.*, 2014; Kanzaki *et al.*, 2012; Kseniya *et al.*, 2022; Liu *et al.*, 2014; Bogdanov & Svinyarov, 2017; Park *et al.*, 2020; Wang *et al.*, 2013). This ligand set features a conjugated diaza five-membered heterocyclic ring structure. One nitrogen atom has an *N*-methyl substituent, and its lone pair is delocalized in the aromatic ring, while the other nitrogen is *sp*<sup>2</sup> hybridized and capable of coordinating Lewis acids, including

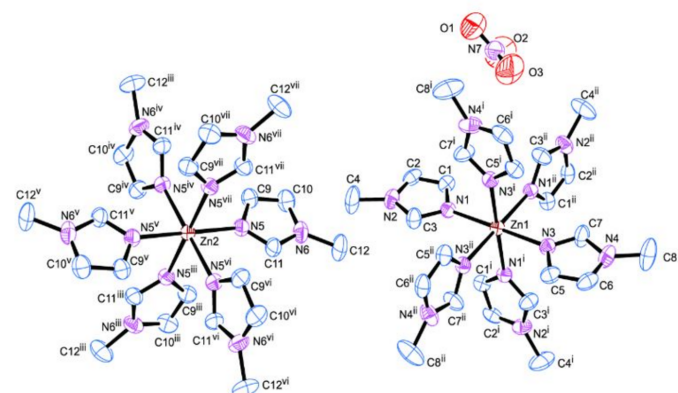


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metal ions. Numerous studies have been published on transition metal ion complexes involving imidazole and its derivatives (Erer *et al.*, 2011; He *et al.*, 2021; Kühl *et al.*, 2011; Jawad & Al-Adilee 2022; Konarev *et al.*, 2018; Neumüller & Dehnicke, 2010; Reedijk *et al.*, 2012; Zhang *et al.*, 2020). The lack of N-methyl group tautomerization enhances the appeal of N-substituted imidazole for the synthesis of novel molecules. The coordination of imidazole derivatives with metal centers has had a positive impact on the development of novel metal complexes with applications in the field of material science (Anjali *et al.*, 2022; Bezvikonnyi *et al.*, 2022; Kempegowda *et al.*, 2021; Rashamuse *et al.*, 2023; Yu *et al.*, 2021). In addition, the use of imidazole derivatives alongside zinc metal ions is an interesting technique to expand the complex repertoire in coordination chemistry. Therefore, our goal was to utilize the *N*-methylimidazole core in conjunction with a zinc metal ion in the presence of ammonia to generate unique complexes with different topologies.



The utilization of 1-methylimidazole as a starting ligand for the synthesis of zinc complexes has been previously explored (Rashidi *et al.*, 2021; Appleton & Sarkar, 1977; Chen *et al.*, 1996; Steichen *et al.*, 2014). In this article, we report the synthesis of a new compound hexakis(1-methyl-1*H*-imidazole- $\kappa$ N<sup>3</sup>)zinc(II) dinitrate, [Zn(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>, which is



**Figure 1**  
Displacement ellipsoid plot of [Zn(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub> showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i)  $y - x, 1 - x, z$ ; (ii)  $1 - y, 1 + x - y, z$ ; (iii)  $-y, x - y, z$ ; (iv)  $y - x, -x, z$ ; (v)  $-x, -y, -z$ ; (vi)  $-y, x + x, -z$ ; (vii)  $y, -x + y, -z$ .]

**Table 1**  
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C12—H12B···O1 <sup>i</sup>	0.98	2.44	3.339 (7)	152
C12—H12C···O3 <sup>ii</sup>	0.98	2.36	3.333 (7)	169
C12—H12A···O2 <sup>iii</sup>	0.98	2.62	3.596 (8)	174

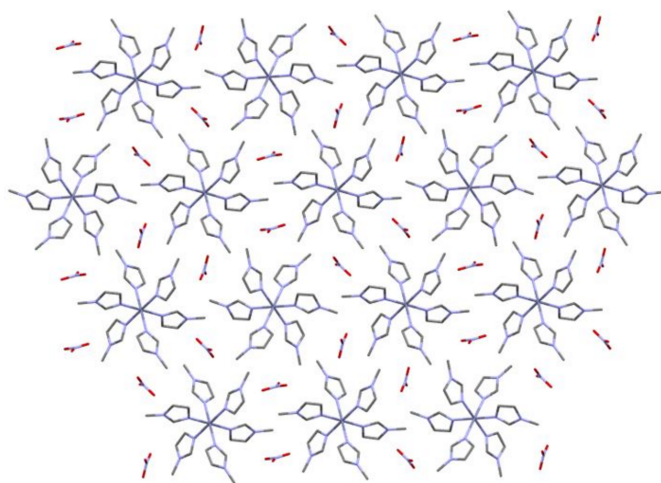
Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + y, -x + 1, z$ ; (iii)  $-x + y, -x + 1, z - 1$ .

synthesized in the manner depicted in the scheme. The structure of the complex was confirmed *via* proton NMR, FTIR, and single-crystal X-ray diffraction.

## 2. Structural commentary

The title compound (Fig. 1) crystallizes in the  $P\bar{3}$  space group with half of a formula unit in the asymmetric unit. There are two crystallographically distinct zinc atoms. One has 1/3 occupancy and is bound to two crystallographically unique 1-methylimidazole ligands and the other has 1/6 occupancy and is bound to one crystallographically unique 1-methylimidazole ligand. One full occupancy nitrate anion is also present in the asymmetric unit.

The full zinc complex ions  $\{[\text{Zn}(N\text{-Melm})_6]^{2+}$ , where *N*-Melm denotes *N*-methylimidazole} exhibit coordination by six *N*-Melm ligands. The ions are in a distorted octahedral coordination environment, demonstrated by N—Zn—N angles close to 90° or 180° depending on their *cis* or *trans* relationship. The Zn—N lengths are 2.182 (2) Å for N1—Zn1, 2.177 (2) Å for N3—Zn1, and 2.179 (2) Å for N5—Zn2. The complex molecule also displays fifteen unique C—N bond lengths ranging from 1.308 (3) to 1.471 (4) Å. The nitrate counter-ion demonstrates O—N—O bond angles of 125.4 (4)° for O2—N7—O3, 118.0 (4)° for O2—N7—O1, and 116.5 (4)° for O3—N7—O1 and N—O bond lengths of 1.202 (5) Å for N7—O2, 1.209 (4) Å for N7—O3 and 1.234 (5) Å for N7—O1.



**Figure 2**  
Packing diagram of the [Zn(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub> complex showing the nitrate cation lying in the void between the cationic complexes.

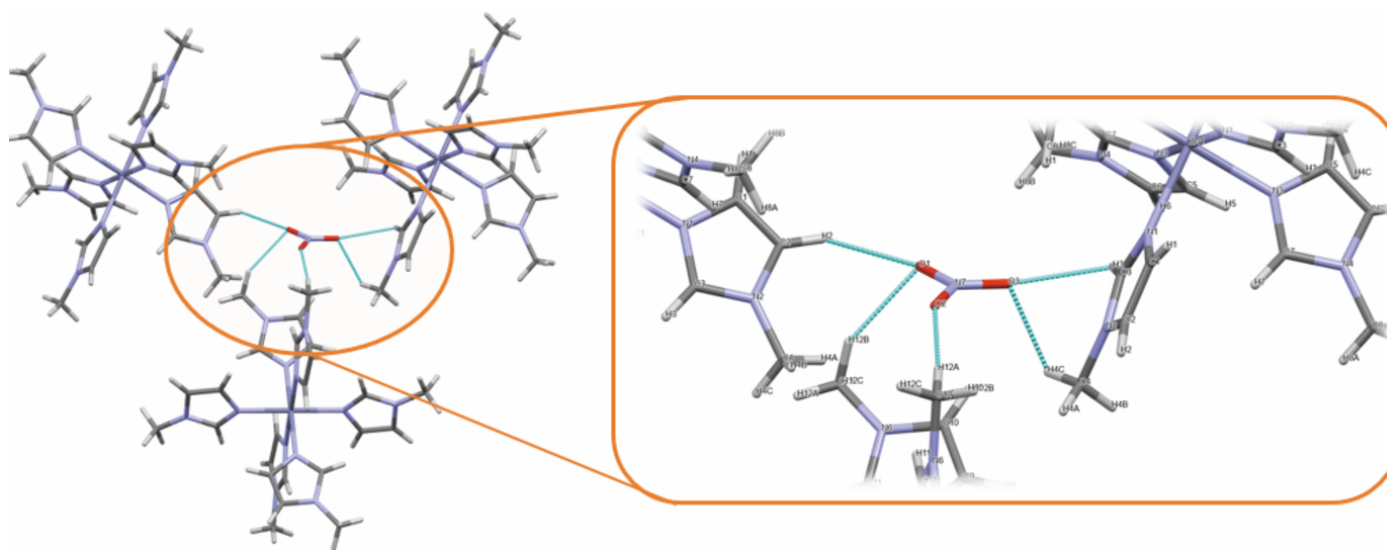

**Figure 3**

Diagram showing interaction between the nitrate ions and *N*-methylimidazole ligands of the title compound with blue dashed lines representing the C—H···O close contacts.

### 3. Supramolecular features

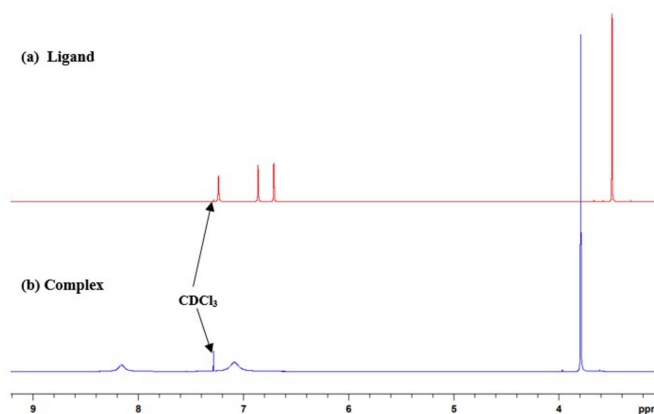
The packing of the title compound is shown in Fig. 2 while Fig. 3 shows the intermolecular interactions in the  $[\text{Zn}(\text{C}_4\text{H}_6\text{N}_2)_6][\text{NO}_3]_2$  complex. In the crystal, the nitrate ions are situated within the cavities created by the  $[\text{Zn}(\text{N-Melm})_6]^{2+}$  cations, serving as counter-ions. The three oxygen atoms of the nitrate ion engage in weak C—H···O interactions (Table 1) with two hydrogen atoms from the imidazole rings and one hydrogen atom from the methyl groups.

### 4. Database survey

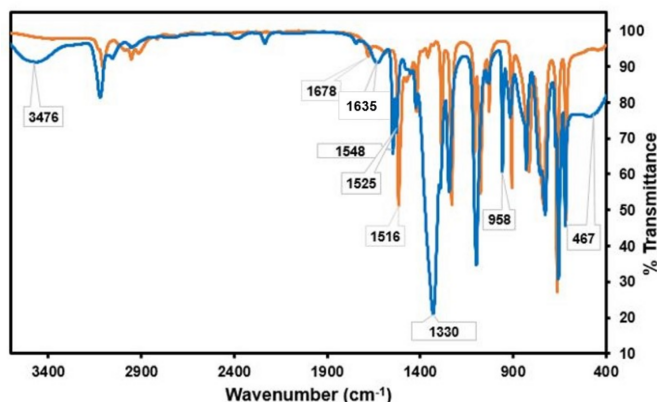
A search of the Cambridge Structural Database (CSD, Version 5.45, update of March 2024; Groom *et al.*, 2016) for  $[\text{Zn}(\text{C}_4\text{H}_6\text{N}_2)_6]$  compounds with nitrate cations resulted in no hits. However, when the search was expanded to include other cationic salts, six relevant ones were found, including a discrete Zn complex with a sixfold coordination. These entries include  $[\text{Zn}(\text{C}_4\text{H}_6\text{N}_2)_6](\text{I})_2$  (CCDC reference: 2347502; Rashidi *et al.*, 2021),  $[\text{Zn}(\text{MeIm})_6](\text{Tf}_2\text{N})_2$ ,  $[\text{Zn}(\text{EtIm})_6](\text{Tf}_2\text{N})_2$ ,  $[\text{Zn}(\text{MeIm})(\text{EtIm})_5](\text{Tf}_2\text{N})_2$ ,  $[\text{Zn}(\text{MeIm})_2(\text{EtIm})_4](\text{Tf}_2\text{N})_2$ , and  $[\text{Zn}(\text{MeIm})_{4.5}(\text{EtIm})_{1.5}](\text{Tf}_2\text{N})_2$  (CCDC references: 978387, 978388, 978389, 978390, and 978391; Steichen *et al.*, 2014) where MeIm is 1-methyl-1*H*-imidazole, EtIm is 1-ethyl-1*H*-imidazole, and  $(\text{Tf}_2\text{N})_2$  is bis(trifluoromethylsulfonyl)imide. The cationic zinc complex paired with iodine anions,  $[\text{Zn}(\text{C}_4\text{H}_6\text{N}_2)_6](\text{I})_2$ , is particularly interesting as it exhibits a very similar structure, similar packing, similar cell parameters, and the same space group as the title compound. Although the zinc ions in the other five complexes had a similar sixfold coordination, the anion involved in these complexes was bis(trifluoromethylsulfonyl)imide, and their crystals exhibited different structures and space groups.

### 5. Synthesis and crystallization

In a typical synthesis, 0.9 g of zinc nitrate hexahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (3.0 mmol), was dissolved in 10 mL of ethanol. A second solution consisting of 0.52 g of *N*-methyl-1*H*-imidazole (6.0 mmol) in 30 mL of ethanol and 2.8 mL of ammonia solution (2.48 mmol) was prepared in parallel. The  $\text{Zn}^{\text{II}}$  solution was poured rapidly into the second solution. The resultant mixture was stirred at room temperature for 10 minutes to complete crystallization. The crystals were collected by centrifugation, filtered, washed three times with ethanol, and dried overnight at room temperature to afford  $[\text{Zn}(\text{C}_4\text{H}_6\text{N}_2)_6][\text{NO}_3]_2$  as light-blue crystals in 67% yield. Analysis calculated for  $\text{C}_{24}\text{H}_{36}\text{N}_{14}\text{O}_6\text{Zn}$ : C, 42.27%; H 5.32%; N, 28.75%; Found: C, 42.71%; H 5.39%; N, 28.56%;  $^1\text{H}$  NMR  $\delta/\text{ppm}$  (400 MHz,  $\text{CDCl}_3$ ): 3.77 (*s*, 3H), 7.06 (*s*, 2H), 8.13 (*s*, 1H);  $^{13}\text{C}$  NMR  $\delta/\text{ppm}$  (101 MHz,  $\text{CDCl}_3$ ): 32.23, 127.99,


**Figure 4**

The superimposed  $^1\text{H}$  NMR spectra of (a) the free *N*-methylimidazole ligand (red) and (b) its corresponding  $[\text{Zn}(\text{C}_4\text{H}_6\text{N}_2)_6][\text{NO}_3]_2$  complex (blue) in deuterated chloroform.



**Figure 5**

The superimposed FTIR spectra of the free ligand *N*-methylimidazole (orange) and its  $[\text{Zn}(\text{C}_4\text{H}_6\text{N}_2)_6](\text{NO}_3)_2$  complex (blue) in the frequency range  $3600\text{--}400\text{ cm}^{-1}$ .

140.04; FTIR  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3121, 1643, 1528, 1516, 1327, 1288, 1231, 1088, 1026, 934, 826, 768, 660, 621.

The overlaid  $^1\text{H}$  NMR spectra of the ligand and zinc complex are shown in Fig. 4. In the proton NMR spectrum of the free *N*-methyl-1*H*-imidazole ligand, there are four sharp signals with the methyl group appearing at 3.47 ppm and the three protons of the imidazole motif appearing at 6.69, 6.84 and 7.21 ppm. However, upon complexation with the zinc ion, the methyl proton shifted to 3.77 ppm, while the imidazole signals are broadened with two protons merged at 7.06 ppm, and the third proton exhibiting a downfield shift to 8.13 ppm. Similar behavior can also be observed in the  $^{13}\text{C}$  NMR spectra, demonstrating complexation.

The comparative FTIR spectra of the free ligand and the zinc complex are presented in Fig. 5. In the spectrum of the zinc complex, a vibrational peak at  $3476\text{ cm}^{-1}$  is observed, which is attributed to the O–H stretching of water molecules as the complex is hygroscopic. The characteristic vibrational peak associated with C=C stretching appears at  $1678\text{ cm}^{-1}$  in the free ligand, but in the complex spectrum, it is shifted to the vibrational frequency of  $1630\text{ cm}^{-1}$ . Furthermore, an intense band at around  $1516\text{ cm}^{-1}$  is evident, which originates from the C=N stretching mode of the imidazole moiety of the free ligand. However, upon zinc coordination, two different vibrational frequencies are observed at  $1545$  and  $1527\text{ cm}^{-1}$ , corresponding to the C=N stretching mode. Notably, both asymmetric and symmetric  $\text{NO}_3$  stretching vibrations at  $1330$  and  $958\text{ cm}^{-1}$  are clearly visible as intense vibrational peaks in the zinc complex spectrum, with both features absent in the free ligand spectrum. Furthermore, a stretching band of Zn–N is observed at a vibrational frequency of  $467\text{ cm}^{-1}$ , providing further evidence of the coordination of zinc ions with the nitrogen atom of the *N*-methylimidazole group.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All C bound hydrogen atoms were placed at idealized positions and refined as riding atoms with

**Table 2**

Experimental details.

Crystal data	
Chemical formula	$[\text{Zn}(\text{C}_4\text{H}_6\text{N}_2)_6](\text{NO}_3)_2$
$M_r$	682.04
Crystal system, space group	Trigonal, $P\bar{3}$
Temperature (K)	173
$a, c$ ( $\text{\AA}$ )	19.1227 (10), 7.4770 (5)
$V$ ( $\text{\AA}^3$ )	2367.9 (3)
$Z$	3
Radiation type	Mo $K\alpha$
$\mu$ ( $\text{mm}^{-1}$ )	0.84
Crystal size (mm)	$0.45 \times 0.34 \times 0.23$
Data collection	
Diffractometer	Bruker D8 Venture Photon CCD area detector
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.660, 0.745
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	119969, 3247, 3073
$R_{\text{int}}$	0.040
$(\sin \theta/\lambda)_{\text{max}}$ ( $\text{\AA}^{-1}$ )	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.032, 0.090, 1.12
No. of reflections	3247
No. of parameters	208
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ( $\text{e \AA}^{-3}$ )	0.51, $-0.36$

Computer programs: *APEX3*, *SAINT-Plus* and *XPREP* (Bruker 2016), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *ORTEP-3 for Windows* and *WinGX* publication routines (Farrugia, 2012) and *PLATON* (Spek, 2020).

isotropic parameters 1.2 or 1.5 times those of their parent atoms. The crystal studied was refined as a two-component twin. H atoms were positioned in idealized locations and refined using a riding model, with isotropic displacement parameters set to 1.2 or 1.5 times those of their respective parent atoms. A twin law was also applied.

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## supporting information

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## Synthesis, characterization, and crystal structure of hexakis(1-methyl-1*H*-imidazole- $\kappa$ N<sup>3</sup>)zinc(II) dinitrate

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### Computing details

#### Hexakis(1-methyl-1*H*-imidazole- $\kappa$ N<sup>3</sup>)zinc(II) dinitrate

##### Crystal data

[Zn(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>

$M_r = 682.04$

Trigonal,  $P\bar{3}$

$a = 19.1227(10)$  Å

$c = 7.4770(5)$  Å

$V = 2367.9(3)$  Å<sup>3</sup>

$Z = 3$

$F(000) = 1068$

$D_x = 1.435$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9720 reflections

$\theta = 3.3\text{--}26.2^\circ$

$\mu = 0.84$  mm<sup>-1</sup>

$T = 173$  K

Block, colourless

$0.45 \times 0.34 \times 0.23$  mm

##### Data collection

Bruker D8 Venture Photon CCD area detector  
diffractometer

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan  
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.660$ ,  $T_{\max} = 0.745$

119969 measured reflections

3247 independent reflections

3073 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 26.4^\circ$ ,  $\theta_{\min} = 2.7^\circ$

$h = -23 \rightarrow 23$

$k = -23 \rightarrow 23$

$l = -9 \rightarrow 9$

##### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.090$

$S = 1.12$

3247 reflections

208 parameters

0 restraints

0 constraints

Primary atom site location: dual - dual-space  
method e.g. SHELXD

Secondary atom site location: dual - dual-space  
method e.g. SHELXD

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 1.2961P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.51$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.36$  e Å<sup>-3</sup>

*Special details*

**Experimental.** Absorption corrections were made using the program SADABS (Sheldrick, 1996) Intensity data were determined on a Bruker Venture D8 Photon CMOS diffractometer with graphite-monochromated Mo K $\alpha_1$  ( $\lambda = 0.71073$  Å) radiation at 173 K using an Oxford Cryostream 600 cooler. Data reduction was carried out using the program SAINT+, version 6.02 (Bruker, 2016) and empirical absorption corrections were made using SADABS (Bruker 2016) Space group assignments was made using *XPREP* (Bruker, 2016). The structure was solved in the *WinGX* (Farrugia, 2012) Suite of programs, using intrinsic phasing through *SHELXT* (Sheldrick, 2015a) and refined using full-matrix least-squares/difference Fourier techniques on F<sup>2</sup> using *SHELXL2017* (Sheldrick, 2015b). Diagrams and publication material were generated using *ORTEP-3* (Farrugia, 2012) and *PLATON* (Spek, 2020).

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refined as a 2-component twin.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> */ <i>U</i> <sub>eq</sub>
C1	0.35319 (17)	0.56158 (16)	0.8432 (4)	0.0370 (5)
H1	0.397348	0.608195	0.894545	0.044*
C2	0.32525 (18)	0.48483 (17)	0.8998 (4)	0.0408 (6)
H2	0.345852	0.467857	0.995698	0.049*
C3	0.25403 (19)	0.48549 (16)	0.6749 (4)	0.0434 (6)
H3	0.214048	0.466944	0.583882	0.052*
C4	0.2155 (3)	0.3487 (2)	0.7945 (6)	0.0742 (12)
H4A	0.221478	0.328911	0.911228	0.111*
H4B	0.235574	0.327455	0.700603	0.111*
H4C	0.158422	0.330563	0.773011	0.111*
C5	0.31191 (18)	0.77017 (19)	0.2309 (4)	0.0408 (6)
H5	0.26636	0.723578	0.183396	0.049*
C6	0.34153 (19)	0.84611 (19)	0.1679 (4)	0.0451 (7)
H6	0.321104	0.862707	0.071015	0.054*
C7	0.41433 (19)	0.84552 (17)	0.3924 (4)	0.0479 (7)
H7	0.455942	0.864052	0.479686	0.057*
C8	0.4553 (3)	0.9812 (2)	0.2607 (6)	0.0860 (15)
H8A	0.510363	0.998228	0.300205	0.129*
H8B	0.431985	1.005728	0.337839	0.129*
H8C	0.456463	0.998554	0.136826	0.129*
N1	0.30848 (13)	0.56202 (13)	0.7012 (3)	0.0321 (4)
N2	0.26215 (16)	0.43720 (15)	0.7926 (3)	0.0437 (6)
N3	0.35725 (12)	0.77013 (12)	0.3735 (3)	0.0330 (4)
N4	0.40615 (19)	0.89350 (16)	0.2712 (4)	0.0510 (7)
Zn1	0.333333	0.666667	0.53840 (6)	0.02973 (13)
C9	0.11565 (17)	0.12401 (17)	0.2960 (4)	0.0397 (6)
H9	0.129642	0.086107	0.340727	0.048*
C10	0.14947 (19)	0.20166 (17)	0.3498 (4)	0.0472 (7)
H10	0.192987	0.227884	0.431476	0.057*
C11	0.06016 (17)	0.17677 (16)	0.1425 (4)	0.0394 (6)
H11	0.027212	0.18447	0.058845	0.047*

C12	0.1277 (3)	0.31748 (19)	0.2617 (6)	0.0669 (10)
H12A	0.101449	0.327601	0.160283	0.1*
H12B	0.185931	0.3554	0.257408	0.1*
H12C	0.105592	0.324868	0.373768	0.1*
N5	0.05952 (13)	0.10858 (12)	0.1642 (3)	0.0353 (5)
N6	0.11268 (16)	0.23427 (14)	0.2519 (4)	0.0453 (6)
Zn2	0	0	0	0.03046 (17)
N7	0.65532 (18)	0.6614 (2)	0.7378 (5)	0.0581 (7)
O1	0.6741 (2)	0.6106 (2)	0.6944 (6)	0.1096 (13)
O2	0.6618 (3)	0.6807 (3)	0.8925 (5)	0.1172 (14)
O3	0.6354 (3)	0.6903 (2)	0.6181 (6)	0.1214 (15)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0432 (14)	0.0399 (13)	0.0321 (13)	0.0239 (11)	0.0013 (11)	0.0015 (11)
C2	0.0552 (16)	0.0522 (15)	0.0319 (12)	0.0395 (14)	0.0082 (12)	0.0065 (11)
C3	0.0529 (16)	0.0332 (13)	0.0378 (14)	0.0167 (12)	-0.0037 (12)	0.0044 (11)
C4	0.099 (3)	0.0314 (16)	0.080 (3)	0.0237 (18)	-0.013 (2)	0.0114 (16)
C5	0.0464 (15)	0.0511 (16)	0.0335 (13)	0.0309 (14)	-0.0040 (12)	0.0000 (13)
C6	0.0587 (17)	0.0621 (18)	0.0342 (13)	0.0449 (15)	0.0066 (13)	0.0111 (12)
C7	0.0596 (18)	0.0318 (13)	0.0474 (16)	0.0192 (13)	-0.0115 (13)	0.0062 (11)
C8	0.126 (4)	0.043 (2)	0.082 (3)	0.037 (2)	0.003 (3)	0.0250 (19)
N1	0.0334 (10)	0.0332 (11)	0.0304 (10)	0.0171 (9)	0.0050 (8)	0.0026 (8)
N2	0.0554 (15)	0.0339 (12)	0.0426 (13)	0.0230 (11)	0.0064 (11)	0.0087 (10)
N3	0.0356 (10)	0.0352 (11)	0.0307 (10)	0.0197 (9)	0.0013 (8)	0.0031 (8)
N4	0.0727 (19)	0.0420 (14)	0.0467 (14)	0.0351 (14)	0.0049 (13)	0.0130 (11)
Zn1	0.02969 (16)	0.02969 (16)	0.0298 (2)	0.01484 (8)	0	0
C9	0.0411 (14)	0.0366 (13)	0.0371 (15)	0.0160 (12)	-0.0034 (11)	-0.0042 (11)
C10	0.0530 (16)	0.0423 (15)	0.0385 (14)	0.0179 (13)	-0.0033 (13)	-0.0024 (12)
C11	0.0407 (13)	0.0328 (12)	0.0433 (14)	0.0173 (11)	0.0000 (12)	-0.0068 (11)
C12	0.083 (3)	0.0314 (16)	0.081 (3)	0.0242 (17)	-0.006 (2)	-0.0153 (16)
N5	0.0340 (11)	0.0311 (10)	0.0395 (12)	0.0153 (9)	0.0015 (9)	-0.0015 (9)
N6	0.0497 (14)	0.0293 (12)	0.0493 (14)	0.0141 (11)	0.0028 (11)	-0.0058 (10)
Zn2	0.0271 (2)	0.0271 (2)	0.0372 (4)	0.01354 (10)	0	0
N7	0.0479 (16)	0.0584 (17)	0.0692 (19)	0.0275 (14)	0.0088 (14)	0.0225 (14)
O1	0.108 (3)	0.088 (2)	0.147 (4)	0.059 (2)	-0.004 (3)	-0.018 (2)
O2	0.156 (4)	0.150 (4)	0.0653 (18)	0.091 (3)	0.029 (2)	0.016 (2)
O3	0.131 (3)	0.113 (3)	0.133 (3)	0.071 (3)	-0.051 (3)	0.016 (3)

*Geometric parameters (Å, °)*

C1—C2	1.355 (4)	C8—H8A	0.98
C1—N1	1.365 (3)	C8—H8B	0.98
C1—H1	0.95	C8—H8C	0.98
C2—N2	1.352 (4)	N1—Zn1	2.182 (2)
C2—H2	0.95	N3—Zn1	2.177 (2)
C3—N1	1.319 (3)	C9—C10	1.351 (4)



C3—N2	1.339 (4)	C9—N5	1.376 (4)
C3—H3	0.95	C9—H9	0.95
C4—N2	1.467 (4)	C10—N6	1.363 (4)
C4—H4A	0.98	C10—H10	0.9486
C4—H4B	0.98	C11—N5	1.308 (3)
C4—H4C	0.98	C11—N6	1.335 (4)
C5—C6	1.352 (4)	C11—H11	0.95
C5—N3	1.375 (3)	C12—N6	1.471 (4)
C5—H5	0.95	C12—H12A	0.98
C6—N4	1.351 (4)	C12—H12B	0.98
C6—H6	0.95	C12—H12C	0.98
C7—N3	1.310 (3)	N5—Zn2	2.179 (2)
C7—N4	1.353 (4)	N7—O2	1.202 (5)
C7—H7	0.95	N7—O3	1.209 (4)
C8—N4	1.458 (4)	N7—O1	1.234 (5)
C2—C1—N1	109.9 (2)	N3—Zn1—N1 <sup>i</sup>	88.74 (8)
C2—C1—H1	125	N3 <sup>i</sup> —Zn1—N1 <sup>i</sup>	179.34 (8)
N1—C1—H1	125	N3 <sup>ii</sup> —Zn1—N1 <sup>i</sup>	88.28 (8)
N2—C2—C1	106.3 (2)	N1 <sup>ii</sup> —Zn1—N1 <sup>i</sup>	91.89 (8)
N2—C2—H2	126.9	N3—Zn1—N1	179.34 (9)
C1—C2—H2	126.9	N3 <sup>i</sup> —Zn1—N1	88.28 (8)
N1—C3—N2	111.6 (3)	N3 <sup>ii</sup> —Zn1—N1	88.73 (8)
N1—C3—H3	124.2	N1 <sup>ii</sup> —Zn1—N1	91.89 (8)
N2—C3—H3	124.2	N1 <sup>i</sup> —Zn1—N1	91.89 (8)
N2—C4—H4A	109.5	C10—C9—N5	110.0 (3)
N2—C4—H4B	109.5	C10—C9—H9	124.8
H4A—C4—H4B	109.5	N5—C9—H9	125.1
N2—C4—H4C	109.5	C9—C10—N6	105.7 (3)
H4A—C4—H4C	109.5	C9—C10—H10	125.7
H4B—C4—H4C	109.5	N6—C10—H10	128.4
C6—C5—N3	110.2 (3)	N5—C11—N6	111.9 (3)
C6—C5—H5	124.9	N5—C11—H11	124
N3—C5—H5	124.9	N6—C11—H11	124
N4—C6—C5	105.8 (2)	N6—C12—H12A	109.5
N4—C6—H6	127.1	N6—C12—H12B	109.5
C5—C6—H6	127.1	H12A—C12—H12B	109.5
N3—C7—N4	111.0 (3)	N6—C12—H12C	109.5
N3—C7—H7	124.5	H12A—C12—H12C	109.5
N4—C7—H7	124.5	H12B—C12—H12C	109.5
N4—C8—H8A	109.5	C11—N5—C9	104.9 (2)
N4—C8—H8B	109.5	C11—N5—Zn2	128.3 (2)
H8A—C8—H8B	109.5	C9—N5—Zn2	125.97 (18)
N4—C8—H8C	109.5	C11—N6—C10	107.5 (2)
H8A—C8—H8C	109.5	C11—N6—C12	125.5 (3)
H8B—C8—H8C	109.5	C10—N6—C12	127.1 (3)
C3—N1—C1	105.0 (2)	N5 <sup>iii</sup> —Zn2—N5 <sup>iv</sup>	180.00 (9)
C3—N1—Zn1	128.56 (18)	N5 <sup>iii</sup> —Zn2—N5	88.61 (8)

C1—N1—Zn1	126.11 (18)	N5 <sup>iv</sup> —Zn2—N5	91.39 (8)
C3—N2—C2	107.3 (2)	N5 <sup>iii</sup> —Zn2—N5 <sup>v</sup>	91.39 (8)
C3—N2—C4	126.1 (3)	N5 <sup>iv</sup> —Zn2—N5 <sup>v</sup>	88.61 (8)
C2—N2—C4	126.5 (3)	N5—Zn2—N5 <sup>v</sup>	180
C7—N3—C5	105.2 (2)	N5 <sup>iii</sup> —Zn2—N5 <sup>vi</sup>	88.61 (8)
C7—N3—Zn1	128.32 (18)	N5 <sup>iv</sup> —Zn2—N5 <sup>vi</sup>	91.39 (8)
C5—N3—Zn1	126.43 (19)	N5—Zn2—N5 <sup>vi</sup>	91.39 (8)
C6—N4—C7	107.8 (3)	N5 <sup>v</sup> —Zn2—N5 <sup>vi</sup>	88.61 (8)
C6—N4—C8	126.0 (3)	N5 <sup>iii</sup> —Zn2—N5 <sup>vii</sup>	91.39 (8)
C7—N4—C8	126.1 (3)	N5 <sup>iv</sup> —Zn2—N5 <sup>vii</sup>	88.61 (8)
N3—Zn1—N3 <sup>i</sup>	91.09 (8)	N5—Zn2—N5 <sup>vii</sup>	88.61 (8)
N3—Zn1—N3 <sup>ii</sup>	91.09 (8)	N5 <sup>v</sup> —Zn2—N5 <sup>vii</sup>	91.39 (8)
N3 <sup>i</sup> —Zn1—N3 <sup>ii</sup>	91.09 (8)	N5 <sup>vi</sup> —Zn2—N5 <sup>vii</sup>	180.00 (8)
N3—Zn1—N1 <sup>ii</sup>	88.28 (8)	O2—N7—O3	125.4 (4)
N3 <sup>i</sup> —Zn1—N1 <sup>ii</sup>	88.73 (8)	O2—N7—O1	118.0 (4)
N3 <sup>ii</sup> —Zn1—N1 <sup>ii</sup>	179.34 (8)	O3—N7—O1	116.5 (4)
N1—C1—C2—N2	-0.4 (3)	C5—C6—N4—C7	0.3 (3)
N3—C5—C6—N4	0.5 (3)	C5—C6—N4—C8	-176.3 (4)
N2—C3—N1—C1	0.1 (3)	N3—C7—N4—C6	-1.1 (4)
N2—C3—N1—Zn1	173.38 (18)	N3—C7—N4—C8	175.5 (4)
C2—C1—N1—C3	0.2 (3)	N5—C9—C10—N6	1.0 (3)
C2—C1—N1—Zn1	-173.31 (17)	N6—C11—N5—C9	-0.2 (3)
N1—C3—N2—C2	-0.3 (3)	N6—C11—N5—Zn2	-170.42 (18)
N1—C3—N2—C4	-175.6 (3)	C10—C9—N5—C11	-0.6 (3)
C1—C2—N2—C3	0.4 (3)	C10—C9—N5—Zn2	170.0 (2)
C1—C2—N2—C4	175.7 (3)	N5—C11—N6—C10	0.8 (3)
N4—C7—N3—C5	1.4 (4)	N5—C11—N6—C12	-179.7 (3)
N4—C7—N3—Zn1	-175.52 (19)	C9—C10—N6—C11	-1.1 (3)
C6—C5—N3—C7	-1.2 (3)	C9—C10—N6—C12	179.4 (3)
C6—C5—N3—Zn1	175.81 (18)		

Symmetry codes: (i)  $\neg y+1, x-\neg y+1, z$ ; (ii)  $\neg x+y, \neg x+1, z$ ; (iii)  $x-\neg y, x, -z$ ; (iv)  $\neg x+y, \neg x, z$ ; (v)  $\neg x, \neg y, -z$ ; (vi)  $\neg y, x-\neg y, z$ ; (vii)  $y, \neg x+y, -z$ .

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C12—H12B $\cdots$ O1 <sup>viii</sup>	0.98	2.44	3.339 (7)	152
C12—H12C $\cdots$ O3 <sup>ii</sup>	0.98	2.36	3.333 (7)	169
C12—H12A $\cdots$ O2 <sup>ix</sup>	0.98	2.62	3.596 (8)	174

Symmetry codes: (ii)  $\neg x+y, \neg x+1, z$ ; (viii)  $\neg x+1, \neg y+1, -z+1$ ; (ix)  $\neg x+y, \neg x+1, z-1$ .